Studies on the precipitation of mercuric sulphide

by Tatsuo YONEKUBO

1. Introduction

It is well known that the precipitate of metallic sulphide is often contaminated with various kinds of impurities when hydrogen sulphide is passed into the solution of metallic salt. For example, mercuric sulphide is contaminated with the mercuric salt or sulphur, the precipitate of the mercuric sulphide being obtained by passing hydrogen sulphide into the solution of the mercuric salt.

Therefore, sodium sulphide or ammonium sulphide is more widely used instead of hydrogen sulphide for the gravimetric quantitative analysis of mercuric salt.

But the hydrogen sulphide method is interesting in the view points of studying the so called coprecipitation phenomena.

Many investigations have been made using the solution of mercuric chloride, which was acidified with hydrochloric acid or sulphuric acid.

It is also well known that mercuric chloride coprecipitates with mercuric sulphide, when hydrogen sulphide is passed into the solution of mercuric chloride, which is strongly acidified with hydrochloric acid. This coprecipitate is supposed to be a double compound of mercuric chloride and mercuric sulphide, which is called mercuric sulphochloride.

In this experiment, hydrogen sulphide was passed into the aqueous solution of mercuric nitrate, which had been acidified with hydrochloric acid or nitric acid.

2. Methods.

About 0.05 or 0.1 molar solution of mercuric nitrate was obtained by using crystallized mercuric nitrate of monohydrated form. A definite volume (10 ml.) of the solution was introduced in a test-tube-shaped glass vessel, which has a ground glass stopper, and was acidified with hydrochloric acid or nitric acid to various kinds of normality. Purified hydrogen sulphide was passed through the solution, the gas being obtained by the action of hydrochloric acid on iron sulphide, and washed well with water. After passing the gas for a definite time, for example, 5 minutes, the vessel was stoppered immediately and shaken a few times, then the precipitate was filtered through a glass filter. The precipitate was washed completely with water.

For the removing of free sulphur, the precipitate was washed with alcohol and then with carbon bisulphide. The carbon bisulphide was removed from the precipitate by washing once with alcohol and once with ether. The ether was driven off by gentle warming and the precipitate then dried at 105°—110°C. to a constant weight and then weighed. To ascertain whether the precipitate of mercuric sulphide was contaminated with mercuric salt, it was dissolved into the solution of sodium sulphide, and mercuric sulphide was reprecipitated from it by adding solid ammonium nitrate, then the weight of the precipitate was compared with the former value.

The solution of sodium sulphide was prepared as following: 20 g. of sodium hydroxide were dissolved into 80ml. of water, one half of the solution was thereafter taken in a vessel, saturated

with purified hydrogen sulphide, then mixed with another half.

The experiments were carried out partly at 45°C. or 70°C., but principally at room temperature of 16° to 20° C.

3. Results and Considerations.

a) In the solution which was acidified with hydrochloric acid, the molar concentration of the salt solution being 0.05192; 10ml. of the solution correspond to 0.12080g. of mercuric sulphide. The results are shown in Table 1.

Table 1.

Concentration of HCl (n.)	Weight of obtained ppt. (g.)	Per cent. for the theoretical value as HgS.
0.5	0.12110	100.25
1.0	0.12114	100.28
3.0	0.12116	100.29
5.0	0.12124	100.36
6.0	0.12250	101.10
7.0	0.12762	105.64

(at room temperature.)

When the concentration of hydrochloric acid was below 5 n., the colour of the precipitate was white in the beginning and then changed to yellow, finally to black. 5minutes were enough to complete the precipitate. The precipitate seemed to contain no mercuric salt by the reprecipitation method from the sodium sulphide solution. Therefore, the precipitate can be weighed directly as mercuric sulphide.

But when the concentration of hydrochloric acid was over 6n., the precipitate differed from the above; namely, the colour of the precipitate remained in light yellow or yellow, and the precipitate became somewhat colloidal, which took long time for filtering in the room temperature. When the hydrogen sulphide was passed into the solution, which was kept at 45°C., the precipitated particles became a little larger. They became more granular at 70°C..

The composition of the precipitate differed from that of pure mercuric sulphide ; the coprecipitate of mercuric sulphide with mercuric salt was also recognized here. 5 minutes of passing hydrogen sulphide were not sufficient to obtain constant composition.

b) In the solution which was acidified with hydrochloric acid, the molar concentration of the salt solution being 0.10372; 10ml. of the solution correspond to 0.24132 g. of mercuric sulphide.

The results are shown in Table 2.

Table 2.

Concentration of HCl (n.)	Weight of obtained ppt. (g.)	Per cent. for the theoretical value as HgS
0.5	0.24149	100.07
1.0	0.24203	100.29
3.0	0.24200	100.28
5.0	0.24210	100.32
6.0	0.24956	103.41
7.0	0.25148	104.21

(at room temperature.)

The colour of the precipitate was same as (a). 5 minutes were also enough to complete the precipitate when the concentration of hydrochloric acid was below 5 n., and also able to be weighed as mercuric sulphide.

In the solution which had the normality of over 6n., the precipitate could not obtained in the form of constant composition within this short time; thus, the direct weighing of it as mercuric sulphide seemed to be inadequate.

High temperature also accelerated the growing of the precipitate.

c) In the solution which was acidified with nitric acid, the molar concentration of the salt solution being 0.05083; 10ml. of the solution correspond to 0.11827 g. of mercuric sulphide.

The results are shown in Table 3.

Table 3.

Concentration of nitric acid (n.)	Weight of obtained ppt. (g.)	Per cent. for theoretical value as HgS
0.5	0.11831	100.04
1.0	0.11851	100.29
3.0	0.11873	100.39

(at room temperature.)

When the normality of the nitric acid was below 3 n., mercuric sulphide was considered to precipitate quantitatively, though the solution had oxidizing action due to nitric acid.

But in the solution of higher normality, for instance, in 6 n., a violent exothermic reaction took place, and a large quantity of sulphur separated out which was hard to remove off from the precipitate of the sulphide.

4. Summary

The coprecipitation phenomena, in acidic solution with hydrochloric acid or nitric acid, have been investigated using mercuric nitrate.

Mercuric sulphide was precipitated from the salt solution quantitatively, when the normality of the acidic solution was kept within some range.

5. References

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ポリビニルフオルマールの2,3の性質に就て

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Some Properties of Polyvinylformal

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Acetic acid is a good solvent for polyvinylformal. There was a parallel relation between the soluble property and the acid concentration.

Acetic acid did not attack polyvinyl formal at room temperature, but at boiling point some acetal percentage was lowered, and the solution viscosity was dropped.

Dilute hydrochloric acid attacked acetal radical but solution viscosity was little lowered.

ポリビニルフオルマールの沃度吸着性に就ては別に報告した。[1] 此の性質及び別に報告した合成法[2]と関連して知る必要があつたので，他の2，3の性質に就て検討した処を報告する。